Preparation of Ni–YSZ thin and thick films on metallic interconnects as cell supports. Applications as anode for SOFC

M. Rieu · P. Lenormand · F. Ansart · F. Mauvy · J. Fullenwarth · M. Zahid

Abstract In this work, we propose the preparation of a duplex anodic layer composed of both a thin (100 nm) and a thick film (10 μm) with Ni–YSZ material. The support of this anode is a metallic substrate, which is the interconnect of the SOFC unit cell. The metallic support limits the temperature of thermal treatment at 800 °C to keep a good interconnect mechanical behaviour and to reduce corrosion. We have chosen to elaborate anodic coatings by sol–gel route coupled with dip-coating process, which are low cost techniques and allow working with moderate temperatures. Thin films are obtained by dipping interconnect substrate into a sol, and thick films into an optimized slurry. After thermal treatment at only 800 °C, anodic coatings are adherent and homogeneous. Thin films have compact microstructures that confer ceramic protective barrier on metal surface. Further coatings of 10 μm thick are porous and constitute the active anodic material.

Keywords Sol–gel · Coatings · Ni–YSZ · Anode · SOFC

M. Rieu (✉) · P. Lenormand · F. Ansart
CIRIMAT, Université Paul Sabatier, UMR CNRS 5085, Bat II R1, 118 Route de Narbonne, 31062 Toulouse Cedex 9, France
e-mail: rieu@chimie.ups-tlse.fr

F. Mauvy · J. Fullenwarth
ICMC Bordeaux-CNRS UPR 9048, 87,
Avenue du Dr. A. Schweitzer, Université de Bordeaux 1,
Pessac Cedex 33608, France

M. Zahid
EIFER, Emmy-Noether-Strasse 11, 76131 Karlsruhe, Germany

1 Introduction

During the last 30 years, SOFC (Solid Oxide Fuel Cell) technology has progressed, in order to reduce cost of SOFC stack, in the aim of future commercialization. Actually, the first generation (1G) of planar SOFC configuration (Fig. 1a) used electrolyte as mechanical support, so it needs a sufficient thickness (around 200 μm) to assume this function. Ionic conductivity of the electrolyte (Yttria Stabilised Zirconia, common electrolyte material [1]) increases with temperature and on this configuration, with the important thickness of the electrolyte, a temperature above 1,000 °C is necessary to allow a good cell working.

Due to this problem, electrolyte thickness was then reduced in the second generation (2G) of planar SOFC (Fig. 1b). YSZ thickness is 10–50 μm to allow cell working at 800 °C. 2G SOFC is anode supported, which is also a ceramic compound and its thickness is in the range 200–1,000 μm. Moreover, an advantage is that this decrease of working temperature allows to use metallic interconnects [2], that are cheaper than ceramic interconnect (like $LaCrO_3$) previously used in 1G SOFC.

However SOFC technologies can still be improved. Here, we propose to work on the third SOFC generation (3G). This new generation (Fig. 1c) use metallic interconnects as mechanical cell supports. Active materials (anode, electrolyte, cathode) are ceramic films of lower thickness, limiting the quantity of ceramic matter used, and so reducing the price of the complete cell. Performances are still good because of the electrolyte thickness decreases (some few tens microns). The working temperature is in the range 600–700 °C. Furthermore, with a good mechanical behaviour, the metallic interconnect support is a good electrical conductor to collect current, and also a good thermal conductor allowing a good temperature distribution. Moreover, when assembling single

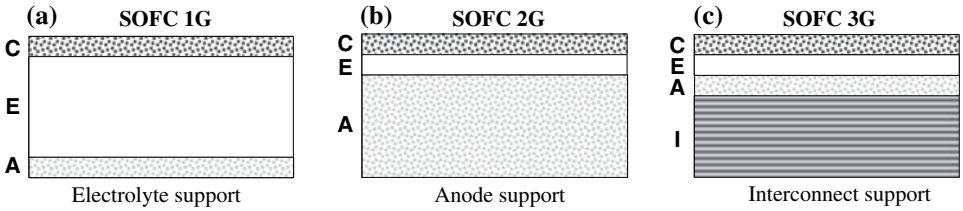

Fig. 1 Various SOFC planar cell configurations

cells in stack, it is easier to weld or connect metallic materials than ceramic ones.

In this prospect, this paper deals with the preparation of anodic layers of 10 µm thick by sol–gel process associated to dip-coating technique on metallic interconnects substrates, which is an adapted route to prepare various oxides films at low temperature with controlled morphology [3, 4]. Anodic material is Ni–YSZ because this cermet is well-known and is the most commonly used [5]. Performances improvement of Ni–YSZ needs electrochemical properties optimization. We propose to optimize microstructure and both phases (Ni and YSZ) distribution by using original elaboration method (sol–gel synthesis and slurries) so that SOFC systems become economically competitive. Film microstructure will depend on several parameters corresponding to either suspension nature (solvent, concentration, rheology), substrate (surface, topography), dip-coating technique (withdrawal speed) and thermal treatment. A control of these experimental parameters will allow to obtain homogeneous and adherent micronic layers with controlled porosity and thickness. However, the use of metallic material as cell support restricts some parameters and in particular sintering temperature of anodic material. Indeed, a heat thermal treatment above 800 °C would degrade metal support. It will thus be necessary to consolidate and sinter anodic coating on the interconnect at relatively low temperature.

So, we propose to prepare a duplex microstructured anode (Fig. 2). To begin with, we first consider preparation of an anodic interfacial thin layer. This thin film will make it possible to better check the wettability of the substrate, to improve the adhesion of a further thicker anodic layer and to help the accommodation of mechanical stresses between

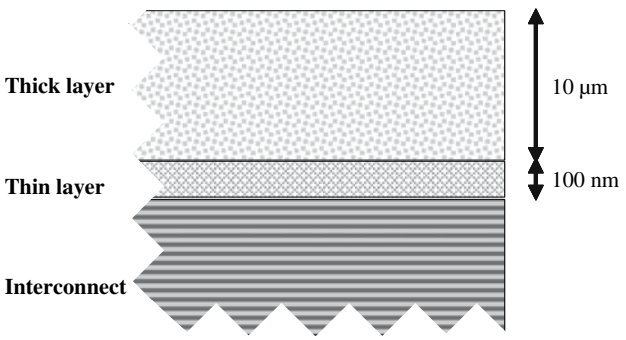

Fig. 2 Duplex anodic system on interconnect cell support

ceramic (anode) and metallic (interconnect) materials. Then, we will optimize the processing of composite powders YSZ–NiO synthesized by sol–gel, in order to obtain a stable slurry. The deposits will be carried out by dip-coating the metallic substrate into the suspension. After thermal treatment at 800 °C, anodic coatings will then be characterized.

2 Experimental

In this work, we propose to prepare a Ni–YSZ duplex anode coating on metallic substrates, which are ferritic stainless steels (F18TNb) manufactured by the UGINE company.

In order to elaborate anodic interfacial films, an alkoxide sol is synthesized [6]. Precursors as zirconium n-propoxide (Aldrich, 70 wt%), n-propanol (Acros organics +99%), yttrium nitrate (Acros Organics 99.9%), nickel nitrate (Acros Organics 99%), acetylacetone (acac, Acros Organics +99%) and water were mixed to synthesize sols. The synthesis parameters were the following: $C = 0.1$ mol/L for the zirconium n-propoxide concentration, $R' = [acac]/\{[Zr] + [Y]\} = 0.7$ for the complexing agent ratio and $W' = [H_2O]/\{[Zr] + [Y]\} = 30$ for the hydrolysis ratio. The nickel precursor quantity insert in the sol corresponds to 50% Ni vol obtained after reduction treatment in the final material. The obtained sol is clear and homogeneous.

Thick films are obtained by a dip-coating process in a slurry composed of YSZ–NiO composite powders which are previously synthesized by a sol–gel polymeric route [6], derived from Pechini process [7]. Precursors were zirconyl nitrate (Acros Organics 99.5%), yttrium nitrate (Acros Organics 99.9%) and nickel nitrate (Acros Organics 99%). The initial concentration was adjusted at $C_{YSZ} = 0.2$ mol/L compared to the polymer matrix volume. The quantity of nickel is also kept at 50 vol% Ni after reduction treatment in the final material. The polymeric sol was obtained by polymerization and polycondensation reactions between hexamethylenetetramine (HMTA, Acros Organics 99%) and acetylacetone (acac, Acros Organics +99%) in acetic acid (VWR) media. The molar ratio between HMTA and acac was 1:1. After heat treatment at 800 °C—2 h, obtained powders consist of two kinds of particles: some small spheres of diameter 30 nm corresponding to YSZ and other faceted particles of 100 nm, which correspond to NiO. There is a good dispersion between the two phases.

Slurries are prepared by addition of these NiO–YSZ powders, under mechanical stirring, in an azeotropic mixture MEK–EtOH (methylethylketone–ethanol) with a polyester-phosphate (MELIORAN P312, CECA) additive used as dispersant.

In order to have stable slurries, Zeta potential instrument (Zetasizer 300HS, Malvern Instruments Ltd.) is used to determine surfacic charges and to adjust the quantity of dispersant to add into suspensions.

Both surface roughness of substrates and thickness of thick films are measured by optical interferometry device ("New View 100" ZYGO Corp).

Structural and microstructural analyses on composite powders and films were achieved, at room temperature, by X-ray diffraction using a D4 ENDEAVOR (BRUKER) diffractometer with the Cu Kα radiation, and Scanning Electron Microscopy (JEOL JSM 6700F).

Electrical conductivity experiments were performed using the four probe method. Four gold wires ($\phi = 0.1$ mm) were connected to the sample using gold paste. The applied current was 10 mA (current density J $\approx$ 100 mA·cm^{-2}). Reducing atmospheres surrounding the sample were obtained by flowing a mixture of hydrogen and water vapour into the sample chamber. Hydrogen is produced by water electrolysis (Dominik Hunter), and humidified by passing through a bubbler. After reduction at 800 °C, the electrical conductivity of the Cermet pellets was measured versus temperature in hydrogen:water (97:3) gas mixture.

3 Results

3.1 Metallic substrate

We use ferritic stainless steel as substrate. The chemical composition of this steel, manufactured by UGINE, is given in Table 1. This steel has many advantages like a fairly good corrosion resistance provided by the formation of protective oxides like Cr_2O_3 and it has good mechanical properties at high temperature. Steel has to be gastight. As we can see on Fig. 3, the steel presents some anfractuosities on the surface, but it is dense. Average roughness coefficient of these steels is Ra = 0.4 µm.

3.2 Thin film

Composite films have been directly deposited onto metallic substrates by dip-coating of an alkoxide sol [6]. Various withdrawal speeds have been investigated: between 1 and 40 cm·min^{-1}. After dipping, the film is heat treated at 800 °C during 2 h. A withdrawal speed of 5 cm·min^{-1} has been chosen as the best compromise to keep homogenous layers on a macroscopic scale.

SEM micrographs reported on Fig. 4 show the composite film microstructure. Film appears continuous, adherent and homogeneous. Roughness of thin film has been measured and the average coefficient is Ra = 0.4 µm, which is the same as substrate before deposit, that is to say the upper layer duplicates steel surface. These thin films are around 100 nm thick as we can see on the cross-section micrograph of a layer deposited on dense YSZ substrate (Fig. 4). They are composed of small spheres of diameter 30 nm, with a good arrangement and a compact microstructure. This kind of microstructure is commonly obtained by sol–gel route and in this range of annealing temperature, the microstructural evolution of the coating is not influenced by the interface substrate/layer [8, 9]. However, it is impossible to precisely separate YSZ and NiO grains, but we have determined crystallite sizes of this composite. They were calculated from XRD pattern using the Williamson and Hall relation, and we see that YSZ and NiO are composed of elementary particles (crystallites) of 30 nm of diameter.

Table 1 Steel F18TNb chemical composition

wt%	C	Mn	Si	Ni	Cr	N	Ti	Nb	S ppm
F18TNb	0.012	0.208	0.58	0.110	17.73	0.015	0.153	0.499	29

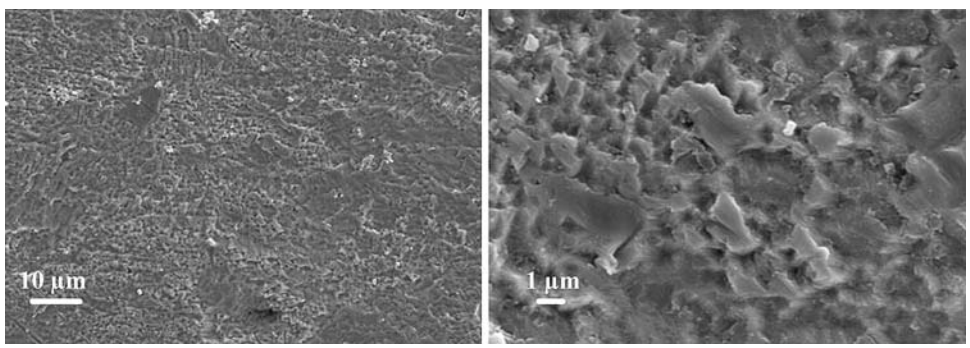

Fig. 3 SEM micrographs of steel surface

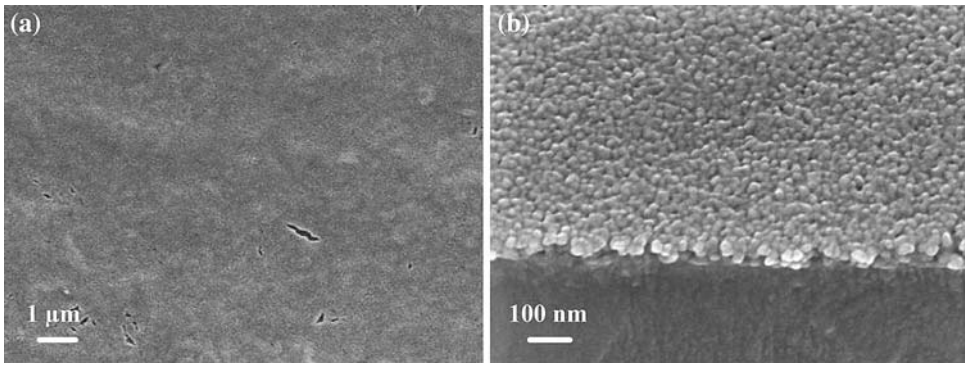

Fig. 4 SEM micrographs of thin alkoxide film after annealing at 800 °C during 2 h: (**a**) surface, (**b**) cross-section

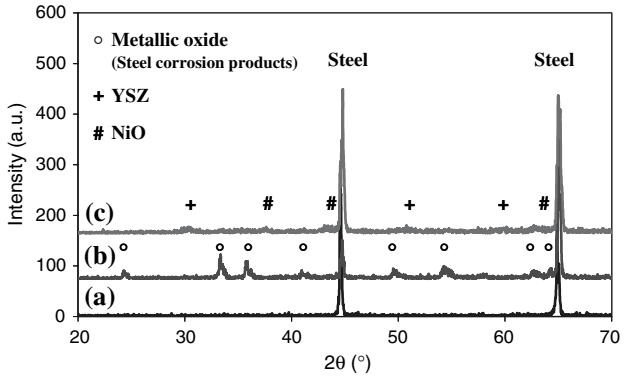

Fig. 5 XRD patterns of (**a**) Steel F18TNb, (**b**) Steel F18TNb annealed at 800 °C—2 h in air, (**c**) Steel F18TNb + thin alkoxide film annealed at 800 °C—2 h in air

As we can see in Fig. 5, steel used as interconnect corrodes itself under air atmosphere at 800 °C during 2 h. But when steel is covered by an YSZ–NiO thin film, the compactness of the layer reduces oxygen diffusion and so it limits the formation of steel corrosion products. That is an important characteristic of such coatings where compact particles organization confers an anticorrosion property of metallic substrate.

Usually, steels used as interconnects need to be coated to limit corrosion. However, these coatings are spinel phase like $(Mn,Co)_3O_4$ [10], perovskite like $LaCrO_3$ or (La,Sr)-CoO_3 [11, 12], or coatings with reactive element oxides like Y_2O_3 [13]. These coatings improve performances of the steel because of the reduction of corrosion products. But we have not found any NiO–YSZ coating protective against corrosion in the literature and this offers new prospects for such metallic substrates.

3.3 Optimization of slurry composition

As we can see on Fig. 6, the composite powder consists of agglomerates constituted of two types of particles: YSZ spheres of 30 nm and NiO faceted particles of 100 nm. In order to desagglomerate such powders and to be able to stabilize slurries and to avoid sedimentation, composite powder is mechanically milled for 1 h. Then the composite powder is first dispersed in MEK–EtOH (60–40) azeotropic mixtures by using a commercial dispersant (P312). This dispersive solvent and dispersant were chosen according to previous optimization work on the formulation of slurries for tape-casting process [14, 15].

In order to obtain a homogeneous and stable suspension, dispersant ratio has been discussed. Several tests have been performed in the range 0–3% in weight. P312 commercial dispersant was first dispersed in the azeotropic mixture and then powder was added under constant mechanical stirring. Zeta potential measurements are reported in Fig. 7, powder concentration for these measurements is 0.1 mg/mL, pH of suspensions is around 6. We see that the best dispersant ratio

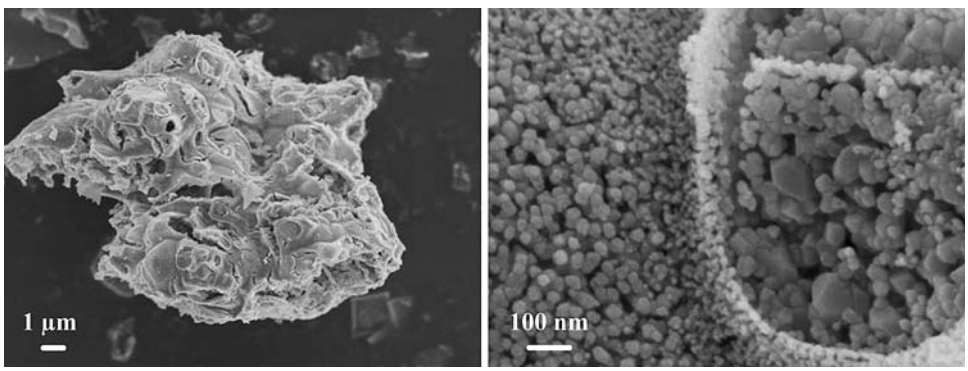

Fig. 6 SEM micrographs of composite powder (NiO–YSZ) after calcination at 800 °C during 2 h

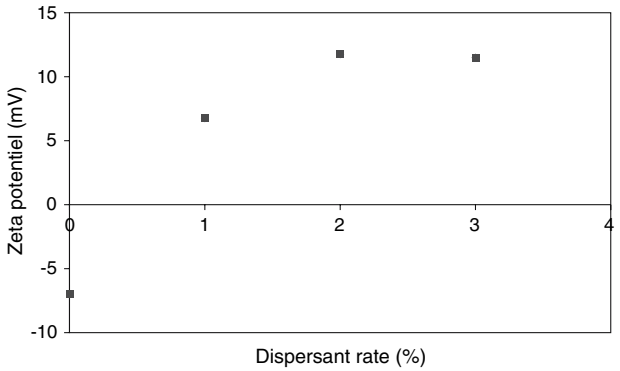

Fig. 7 Zeta potential measurements performed on suspensions containing composite powders with different amounts of dispersant

is in the range 2–3%. By sedimentation tests, we try to refine this dispersant ratio. Sedimentation tests were performed by pouring 50 mL of a given suspension into a 50 mL graduated Pyrex glass cylinder. For this test, 1 g of composite powder was dispersed in MEK–EtOH solution with different amounts of dispersant (1.5; 2; 2.5 and 3%). With a value of 2.5 wt% of dispersant, the suspension is very stable. Even after 72 h, no sediment volume was observed.

3.4 Thick film

After this first step of optimization, we have defined the elaboration conditions of thick films: 67 wt% of composite powder, 33 wt% of MEK–EtOH and a dispersant concentration of 2.5% (in reference to composite powder mass). First tests of films processing from this suspension have shown that they are neither homogeneous nor adherent. To improve that, we add alkoxide sol in the suspensions. The composition of the slurry is 50 wt% of composite powder, 25 wt% of MEK–EtOH with 2.5% of dispersant (include in powder mass) and 25 wt% of alkoxide sol. The substrate is then dip-coated in the slurry and withdrawn at 20 $cm \cdot min^{-1}$ before sintering at only 800 °C during 2 h. As we can see on the micrographs in Fig. 8, the obtained film is continuous, adherent, porous, homogeneous and about 10 µm thick. We can see small particles coated on bigger ones; particles from alkoxide sol play a key role of cement of composite powders.

We have then controlled by XRD that phases were pure (Fig. 9). Alkoxide sol allows an "in situ" growth of NiO and YSZ, which consolidate the layer.

After reduction under H_2 at 800 °C during 1 h in order to obtain the cermet (Ni–YSZ) coating, the thick film is still adherent and homogeneous. As we can see in Fig. 10, thickness is still around 10 µm. First, there are only some cracks which can be eliminated by adjusting the proportion of alkoxide sol and second, film is more porous than before reduction.

Furthermore, XRD pattern, reported in Fig. 9, shows that NiO is reduced in Ni, and YSZ remains stable under reducing atmosphere.

So, we have elaborated with success a duplex anodic layer on metallic substrate. With a thermal treatment at only 800 °C, we have obtained adherent and homogeneous

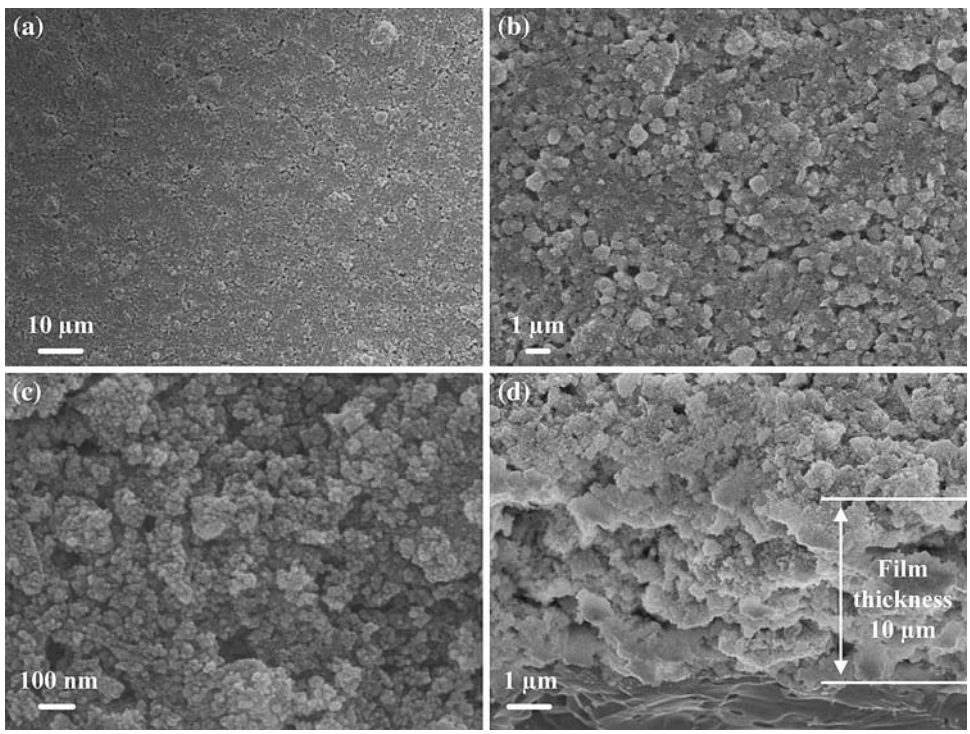

Fig. 8 SEM micrographs of thick composite film after annealing at 800 °C during 2 h: (**a**, **b**, **c**) surface, (**d**) cross-section

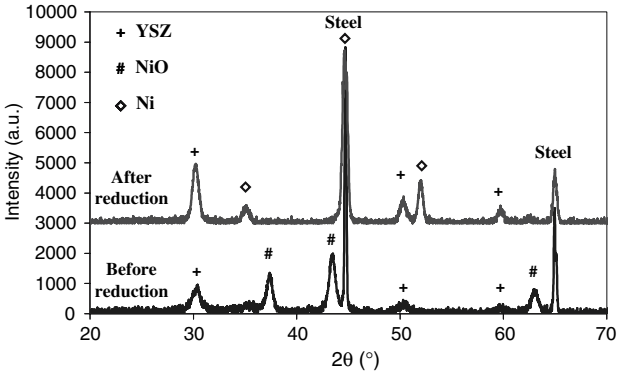

Fig. 9 XRD pattern of thick composite film annealed at 800 °C—2 h in air and of thick cermet film reduced at 800 °C—1 h in hydrogen

anodic coatings. Nowadays, anodes are still mainly bulk materials [16], excepted some anode functional layers 5–10 µm thick elaborated by screen printing [17] or pressurized spray process [18], but they use a heat thermal treatment at 1,300 °C. In our knowledge, no thick anodic layer has been elaborated on metallic support.

3.5 Electrical conductivity

Electrical conductivity measurements were performed on massive anode. For that, composite powder, previously synthesized by the modified Pechini process, is pressed into pellets under 350 MPa and sintered in air at 1,200 °C during 2 h. Pellets are then reduced in hydrogen at 800 °C during 1 h. As we can see on micrographs reported in Fig. 11, there is a homogenous distribution of the two phases. The electrical conductivity has been measured with the four-point technique. The conductivity value is in the range of 500–600 $S \cdot cm^{-1}$ at 700 °C (Fig. 12) and increases when the temperature decreases. This result is promising for a IT-SOFC application. That is a very good conductivity since the required conductivity is only 200 $S \cdot cm^{-1}$ at working temperature [19, 20].

4 Conclusion

An alternative experimental process which combines both dip-coating method and optimized slurries technology was developed in this work to prepare NiO–YSZ duplex systems (thin film + thick film) on metallic substrates. We have first obtained, at 800 °C, NiO–YSZ thin film (100 nm), continuous, compact and protective against corrosion. Then to elaborate thick film, the dip-coating media consists of sol–gel synthesized NiO–YSZ powders in suspensions in organics compounds, which contain a proportion of alkoxide sol. After calcinations at only 800 °C, the obtained layers are continuous, homogeneous and adherent. The layers microstructure is significantly porous. The films thickness is around 10 µm, which is in

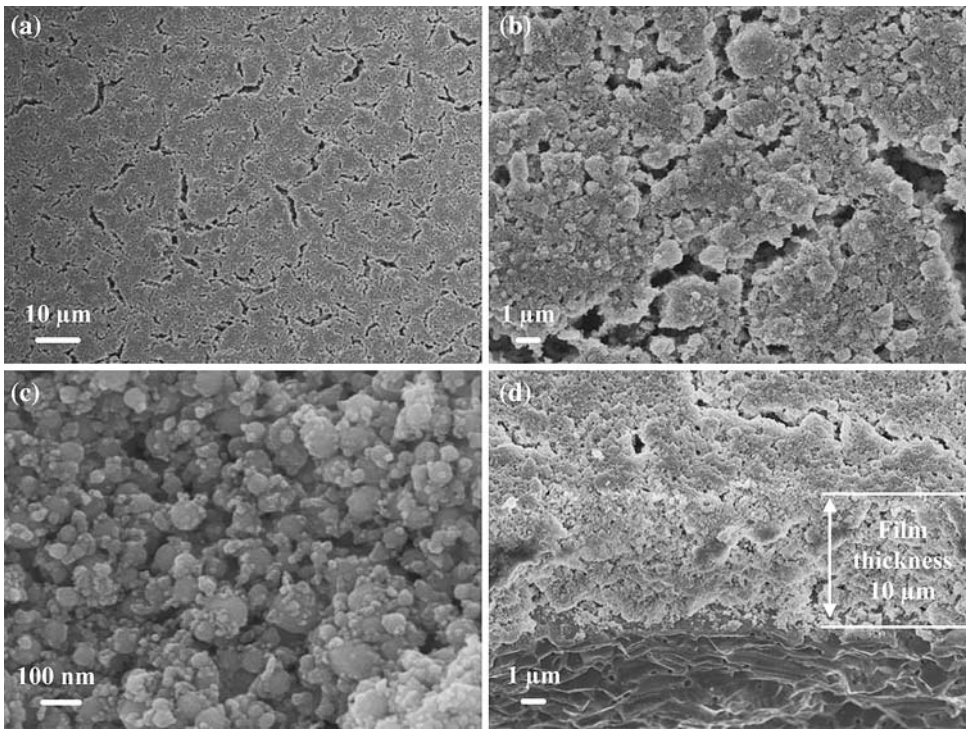

Fig. 10 SEM micrographs of thick cermet film after reduction at 800 °C—1 h in hydrogen: (**a**, **b**, **c**) surface, (**d**) cross-section

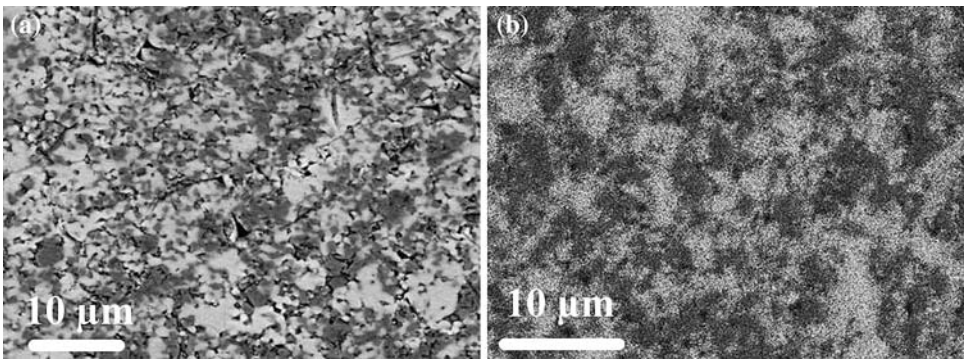

Fig. 11 SEM composition micrographs of cermet pellets (YSZ in light and NiO and Ni in dark): (**a**) after sintering at 1,200°C—2 h in air, (**b**) after reduction at 800 °C—1 h in hydrogen

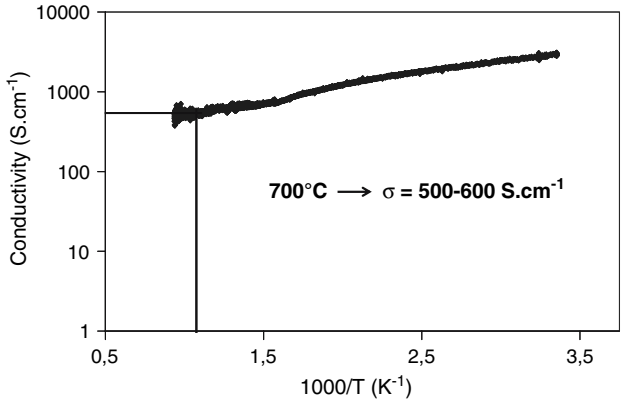

Fig. 12 Electrical conductivity measurements performed by four-point-probe technique on cermet pellet containing 60 vol% Ni

good agreement with requirements for 3G-SOFC anode working at 700 °C. The originality of this work is the development of a low cost process to prepare such anodic layers on interconnects cell supports.

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